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(21) International Application Number: PCT/GB98/03056 (22) International Filing Date: 9 October 1998 (09.10.98) (30) Priority Data: 9721588.3 10 October 1997 (10.10.97) GB (71) Applicant (for all designated States except US): E.I. DUPONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): PERRING, Keith, Douglas [GB/GB]; 14 Malvern Road, Ashford, Kent TN24 8HS (GB). CLEMENTS, Christopher, Francis [GB/GB]; Inveresk, Lookers Lane, Saltwood, Hythe, Kent CT21 5HW (GB). MACMASTER, Angus, Peter [GB/GB]; The Barn, Robus Ceramics, Evington Park, Hastingleigh, Nr Ashford, Kent TN25 5JH (GB). PALMEN, Raymond [NL/CH]; 3, chemin de Passoret, CH-1234 Vessy (CH). JOHN, Olivier, William [CH/CH]; 7, rue Monnier, CH-1207 Geneva (CH). (74) Agents: KUHNEN, Rainer, A. et al.; Alois-Steinecker-Strasse 22, D-85354 Freising (DE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR TEXTILE TREATMENT FOR SPANDEX CONTAINING FABRICS		
(57) Abstract A method of treating textile which is yarn or fabric containing spandex fibres, comprising contacting the textile with a perfume so that the perfume is deposited on the fabric. The perfume contains a mixture of fragrance materials which preferentially deposit on the spandex fibres. The yarn of fabric may be made up into garments.		

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METHOD FOR TEXTILE TREATMENT FOR SPANDEX CONTAINING FABRICS

This invention relates to the treatment of textiles containing spandex fibres.

At the present time, many garments are made from fabric which contains a mixture of fibres, a proportion of which are elastic, so that the fabric has the ability to stretch and to recover from stretch. Spandex fibres are commonly used for this purpose. The term "Spandex" has been adopted as a generic term by the United States Federal Trade Commission to denote a manufactured fibre in which the fibre-forming substance is a long chain synthetic polymer composed of at least 85% of a segmented polyurethane. A discussion of such fibres can be found in "History of Spandex Elastomeric Fibres" by A.J. Ultee, which is a chapter starting at page 278 in *Man-Made Fibres: Their Origin and Development*, edited by R.V. Seymour and R.S. Porter, Elsevier 1993. Spandex fibres are also referred to as "elastane" or "elasthane" fibres.

Another discussion of such fibres is found under the heading "Segmented Polyurethanes" at page 613 of *Handbook of Textile Fibres* by J. Gordon Cook, 5th Ed. Merrow Publishing Company 1984. Further

description of elastanes and their applications can be found in "Synthesefasern: Grundlagen, Technologie, Verarbeitung und Anwendung", B von Falkei (editor), Verlag Chemie (1981). Commercially available elastanes
5 are well known, in particular as sold under the name LYCRA®, a registered trade mark of DuPont de Nemours and Company. Patents relating to such fibres include US-A-5000899, US-A-5288779 and US-A-5362432.

The deposition of perfume onto garments and
10 other fabrics during laundering has been established for many years. Perfume is incorporated into laundry products such as detergent compositions for fabric washing and rinse conditioners for softening the fabrics.

15 Although the perfume serves to cover the base odour of such a product and to give the unused product an attractive fragrance, it also deposits on the fabric.

Certain perfumes have the ability to provide
20 deodorant action against body odour, either when directly applied to human skin, or when included in a laundry product. Such perfumes are described in EP-B-3172, US-A-4304679, US-A-4278658, US-A-4134838, US-A-4288341 and US-A-4289641, US-A-5482635 and US-A-
25 5554588.

Summary of the Invention

We have now found that a number of fragrance materials used in perfumery are able to deposit and then be retained better on spandex fibres than on a
5 number of other textile fibres.

Delivery of fragrance materials to fabric can take place during washing, as is well known. The present invention appreciates that the application of perfume to textiles containing spandex fibres can be
10 utilised in the treatment of textiles which are newly made - that is to say textile goods which have never been worn as garments by a consumer.

Therefore in one aspect the present invention provides a method of treating textile which
15 is yarn or fabric containing spandex fibres, comprising contacting the textile with a perfume so that the perfume is deposited on the fabric. Preferably, the fabric is unworn. It may have been made up into a garment. (1)

20 In a related second aspect, the invention provides textile which is yarn or fabric containing spandex fibres, having perfume deposited on the textile. Preferably, the fabric is unworn. It may have been made up into a garment. (2)

25 We have observed that a range of fragrance materials deposited on such textiles will still be

perceptible on the fabric, even after several washes of the fabric using laundry products with a different perfume, or none.

The invention also provides use of a perfume composition in the treatment of textile which is yarn or fabric containing spandex and other fibres, to deposit fragrance materials at a greater concentration on the spandex fibres than on the other fibres. Preferably, the fabric is unworn.

(3)

In significant forms of this invention, the perfume used to treat the textile (or the combination of fragrance materials deposited thereon) is a deodorant perfume. Then when the textile is made into a garment, that garment will have an in-built deodorant property.

(4)

Detailed description

The various aspects of this invention, preferred forms and materials useful therein will now be discussed in greater detail.

20 Textiles

The textiles to which this invention relates include spandex fibres. As mentioned earlier, this term denotes a manufactured fibre in which the fibre forming substance is a long chain synthetic polymer compound composed of at least 85% of a segmented polyurethane.

Thus the polymer which is spun into spandex fibres is a copolymer incorporating urethane linkages. Generally the polymer contains so-called soft (i.e. lower melting) segments which may be polyalkylene ethers or polyesters and so-called hard (i.e. higher melting) segments which are portions derived from the reaction of an isocyanate and a chain extender which is typically a diamine.

The soft segments may be poly(tetramethylene)ethers, possibly containing substituted tetramethylene glycol residues as described in US-A-5000899. Organic diisocyanates which may be used include conventional diisocyanates, such as diphenylmethane-4,4'-diisocyanate, also known as methylene-bis(4-phenylisocyanate) or "MDI", 2,4-tolylene diisocyanate, methylene-bis(4-cyclohexylisocyanate), isophorone diisocyanate, tetramethylene-p-xylylene diisocyanate, and the like. MDI is preferred.

Chain extenders used in producing the hard segment of the fibres preferably include one or more of ethylenediamine (EDA), 1,3-propylenediamine, 1,4-cyclohexanediamine, hydrogenated m-phenylenediamine (HPMD), 2-methylpentamethylene diamine (MPMD) and 1,2-propylene diamine. More preferably, the chain extender is one or more of ethylenediamine, 1,3-

propylenediamine, and 1,4-cyclohexanediamine,
optionally mixed with HPMD, MPMD and/or 1,2-
propylenediamine.

Spandex fibres with poly(tetramethylene)
5 ethers as the soft segments are marketed by DuPont de
Nemours International S.A. under the registered trade
mark LYCRA® of DuPont de Nemours and Company.

Spandex fibres are generally mixed with
other fibres such as cotton, polyamide, wool,
10 polyester and acrylics and made into yarn which is
then made into fabric. The content of spandex fibres
is usually in a range from 0.5% by weight of the yarn
or fabric up to 50%, more usually from 1 to 30% by
weight of the yarn or fabric.

15 A wide range of garments may contain spandex
fibres in the fabric, including active sports wear,
intimate apparel, hosiery and a variety of ready to
wear casual clothing.

The textiles which are treated with a
20 perfume composition prior to wearing may be yarn which
is later made into fabric, or may be fabric in the
form of a web or lengths from a web which have not yet
been made into garments, or may possibly be garments.

Preferably the treatment with a perfume
25 composition is carried out while treating with other
material in a conventional process step, especially a

wet stage in which the yarn or fabric is treated with a finishing agent to improve its hand or appearance.

However, the perfume composition may be included directly into the spandex fibre. A fabric
5 may be made using the spandex fibre alone.
Alternatively, the spandex fibre may be covered or mixed with other fibres and made into a yarn which is then made into fabric.

The materials which may be applied to fabric
10 in a conventional finishing treatment include resins to confer stiffness, fabric stability or permanent press, fabric softeners, flame retardants, fabric brighteners, anti-snap agents, materials to confer soil or stain resistance and water repellants.

15 Techniques which are conventionally used to apply such materials are padding and exhaustion, both well known in the technology of textile manufacture.

Treatment with a perfume composition in accordance with this invention can be carried out by
20 including the perfume composition in the liquor used in a process as above.

The amount of perfume deposited on the fabric in a treatment step carried out on fabric will generally be from 0.001% to 1% by weight of the
25 fabric.

Fragrance materials

We have found that a range of fragrance materials deposit well on, or are retained well on, spandex fibres. Such materials include the following two categories:

5 Category A

hydroxylic materials which are alcohols, phenols or salicylates, with an octanol/water partition coefficient (P) whose common logarithm ($\log_{10}P$) is 2.5 or greater, and a gas chromatographic Kovats index (as determined on polydimethylsiloxane as non-polar stationary phase) of at least 1050.

Category B

esters, ethers, nitriles, ketones or aldehydes, with an octanol/water partition coefficient (P) whose common logarithm ($\log_{10}P$) is 2.5 or greater, and a gas chromatographic Kovats index (as determined on polydimethylsiloxane as non-polar stationary phase) of at least 1300.

The octanol-water partition coefficient (or its common logarithm 'logP') is well known in the literature as an indicator of hydrophobicity and water solubility (see Hansch and Leo, *Chemical Reviews*, 71, 526-616, (1971); Hansch, Quinlan and Lawrence, *J.Organic Chemistry*, 33, 347-350 (1968). Where such values are not available in the literature they may be measured directly, or estimated approximately using

mathematical algorithms. Software providing such estimations are available commercially, for example 'LogP' from Advanced Chemistry Design Inc.

A requirement for $\log_{10}P$ of 2.5 or more calls
5 for materials which are somewhat hydrophobic.

Kovats indices are calculated from the retention time in a gas chromatographic measurement referenced to the retention time for alkanes [see Kovats , *Helv.Chim.Acta* 41, 1915 (1958)]. Indices
10 based on the use of a non-polar stationary phase have been used in the perfumery industry for some years as a descriptor relating to the molecular size and boiling point of ingredients. A review of Kovats indices in the perfume industry is given by T
15 Shibamoto in "Capillary Gas Chromatography in Essential Oil Analysis", P Sandra and C Bicchi (editors), *Huethig* (1987), pages 259-274. A common non-polar phase which is suitable is 100% dimethyl polysiloxane, as supplied for example under a variety
20 of tradenames such as HP-1 (Hewlett-Packard), CP Sil 5 CB (Chrompack), OV-1 (Ohio Valley) and Rtx-1 (Restek).

Materials of low Kovats index tend to be volatile and are not retained well on many fibres.

We have found that when perfumery materials
25 have partition coefficient as above and a relatively high value of Kovats index, deposition and retention

on spandex tends to be greater than on other fibres. Preferably therefore, the perfume composition contains at least 50 wt %, better at least 70 or 80 wt % of materials from the categories above.

5 We have found that there is a particularly high enhancement of deposition and retention on spandex, compared to other fibres, with materials within the above categories and having a Kovats index of not more than 1600. These sub-sets of categories A and B may be termed categories A' and B'. Preferably
10 therefore, the perfume composition contains at least 10 wt%, better at least 20 wt% or 25 wt% of such materials. In some preferred perfumes the amount of fragrance materials from categories A' and B' is at
15 least 40 wt% in total.

 Such fragrance materials are of mid-range volatility (i.e. intermediate between the volatile perfume materials used as "top-notes" and the materials of low volatility which are customarily used
20 as "base notes" in perfumes). These materials of mid-range volatility are often not perceptible on other fabrics such as cotton, polyamide and polyester after washing and drying.

 Category A includes alcohols of general
25 formula ROH where the hydroxyl group may be primary, secondary or tertiary, and the R group is an alkyl or

alkenyl group, optionally branched or substituted,
cyclic or acyclic, such that ROH has partition
coefficient and Kovats properties as defined above.
Alcohols of Kovats index 1050 to 1600 are typically
5 monofunctional alkyl or arylalkyl alcohols with
molecular weight falling within the range 150 to 230.

Category A also includes phenols of general
formula ArOH, where the Ar group denotes a benzene
ring which may be substituted with one or more alkyl
10 or alkenyl groups, or with an ester grouping $-CO_2A$,
where A is a hydrocarbon radical, in which case the
compound is a salicylate. ArOH has partition
coefficient and Kovats index as defined above.
Typically, such phenols with Kovats index 1050 to 1600
15 are monohydroxylic phenols with molecular weight
falling within the range 150 to 210.

A sub-set of fragrance materials which are
particularly preferred are those with a partition
coefficient of 1000 or more, i.e. $\log_{10}P$ of 3 or more,
20 and a Kovats parameter of 1100 up to 1600.

Some examples of hydroxylic ingredients
which fulfil the above criteria for category A' are
listed as a table below. Materials which are in the
particularly preferred sub-set are marked with an
25 asterisk. Semitrivial names are those used in standard
texts known within the perfume industry, particularly:

Common Fragrance and Flavor Materials by Bauer, Garbe and Surburg, VCH Publ., 2nd edition (1990), and *Perfume and Flavour Materials*, Steffen Arctander, published in two volumes by the author (1969).

5	Examples of fragrance materials in category A'
	1-(2'-tert-butylcyclohexyloxy)-butan-2-ol*
	3-methyl-5-(2',2',3'-trimethylcyclopent-3-enyl)-pentan-2-ol*
	4-methyl-3-decen-5-ol*
10	amyl salicylate*
	2-ethyl-4(2',2',3-trimethylcyclopent-3'-enyl)but-2-enol* (Banalol, TM)
	borneol*
	carvacrol*
15	citronellol*
	9-decenol*
	dihydroeugenol*
	dihydrolinalol*
	dihydromyrcenol
20	dihydroterpineol *
	eugenol
	geraniol*
	hydroxycitronellal*
	isoamyl salicylate*
25	isobutyl salicylate*
	isoeugenol*
	linalol
	menthol*
	nerolidol*

	nerol*
	para tert-butyl cyclohexanol*
	phenoxanol*
	terpineol
5	tetrahydrogeraniol*
	tetrahydrolinalol
	tetrahydromyrcenol
	thymol*
	2-methoxy-4-methylphenol (Ultravanil, TM)
10	(4-isopropylcyclohexyl)-methanol*

Some examples of fragrance materials which are in category A but which have Kovats index above 1600 (so as to fall outside category A') are:

- benzyl salicylate
- 15 cyclohexyl salicylate
- hexyl salicylate
- patchouli alcohol
- farnesol

Category B is esters, ketones, aldehydes, nitriles or ethers which have an octanol-water partition coefficient whose common logarithm ($\log_{10}P$) is at least 2.5, and a Kovats index of at least 1300 (non-polar phase).

Ingredients of Category B are of general formula RX, where X may be in a primary, secondary or tertiary position, and is one of the following groups:

-COA, -OA, -CO₂A, -CN or -CHO. The groups R and A are hydrocarbon residues, cyclic or non-cyclic and optionally substituted. In some forms of this invention, category B excludes any material with a free hydroxy group, so that where a hydroxyl group is present, the material should be considered only for Category A membership. Typically, the materials of Category B with Kovats index not exceeding 1600 (which may be called category B') are monofunctional compounds with molecular weights in the range 160 to 230.

A sub-set of particularly preferred fragrance materials within category B' is those with a Kovats parameter falling within the range 1350 up to 1600, and possessing a molecular structure containing a ring, such as phenyl or cycloalkyl.

A number of fragrance materials which fulfil the above criteria for category B' are listed in the table below. Materials which are in the particularly preferred sub-set are marked with an asterisk.

Examples of fragrance materials in category B'	
1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carbaldehyde*	25
1-(5',5'-dimethylcyclohexenyl)-pent-en-1-one*	
2-heptyl cyclopentanone*	

	2-methyl-3-(4'-tert-butylphenyl)propanal	
	2-methylundecanal	
	2-undecenal	
	2,2-dimethyl-3-(4'-ethylphenyl)-propanal	
5	3-(4'-isopropylphenyl)-2-methylpropanal	
	4-methyl-4-phenylpent-2-yl acetate*	
	allyl cyclohexyl propionate*	
	allyl cyclohexyloxyacetate*	
	amyl benzoate*	
10	methyl ethyl ketone trimers	(Azarbre, TM)
	benzophenone*	
	3-(4'-tert-butylphenyl)-propanal	(Bourgeonal, TM)
	caryophyllene*	
	cis-jasmone*	
15	citral diethyl acetal	
	citronellal diethyl acetal	
	citronellyl acetate	
	phenylethyl butyl ether	(Cressanther, TM)
	damascone, alpha-*	
20	damascone, beta-*	
	damascone, delta-*	
	decalactone, gamma-*	
	dihydro isojasmonate*	
	dihydrojasmone*	
25	dihydroterpinyl acetate	
	dimethyl anthranilate*	
	diphenyl oxide*	
	diphenylmethane*	
	dodecanal	
30	dodecen-2-al	
	dodecane nitrile	

	1-ethoxy-1-phenoxyethane	(Efetaal, TM)
	3-(1'-ethoxyethoxy)-3,7-dimethylocta-1,6-diene	(Elintaal Forte (TM)
	4-(4'-methylpent-3'-enyl)-cyclohex-3-enal	(Empetaal, TM)
5	ethyl tricyclo[5.2.1.0~2,6~]decane-2-carboxylate*	
	1-(7-isopropyl-5-methylbicyclo[2.2.2]oct-5-en-2-yl)-1-ethanone*	(Felvinone, TM)
	allyl tricyclodecenyl ether*	(Fleuroxene, TM)
	tricyclodecenyl propanoate*	(Florocyclene, TM)
10	gamma-undecalactone*	
	n-methyl-n-phenyl-2-methylbutanamide*	(Gardamide, TM)
	tricyclodecenyl isobutyrate*	(Gardocyclene, TM)
	geranyl acetate	
	hexyl benzoate*	
15	ionone alpha*	
	ionone beta*	
	isobutyl cinnamate*	
	isobutyl quinoline*	
	isoeugenyl acetate*	
20	2,2,7,7-tetramethyltricycloundecan-5-one*	(Isolongifolanone, TM)
	tricyclodecenyl acetate*	(Jasmacyclene, TM)
	2-hexylcyclopentanone	(Jasmatone, TM)
	4-acetoxy-3-pentyltetrahydropyran*	(Jasmopyrane, TM)
25	ethyl 2-hexylacetoacetate	(Jessate, TM)
	8-isopropyl-6-methylbicyclo[2.2.2]oct-5-ene-2-carbaldehyde	(Maceal, TM)
	methyl 4-isopropyl-1-methylbicyclo[2.2.2]oct-5-ene-2-carboxylate*	
30	methyl cinnamate	
	alpha iso methyl ionone*	
	methyl naphthyl ketone*	

	nerolin
	nonalactone gamma
	nopyl acetate*
	para tert-butyl cyclohexyl acetate
5	4-isopropyl-1-methyl-2-[1'-propenyl]-benzene* (Pelargene, TM)
	phenoxyethyl isobutyrate*
	phenylethyl isoamyl ether*
	phenylethyl isobutyrate*
10	tricyclodecenyl pivalate* (Pivacyclene, TM)
	phenylethyl pivalate* (Pivarose, TM)
	phenylacetaldehyde hexylene glycol acetal*
	2,4-dimethyl-4-phenyltetrahydrofuran (Rhubafuran, TM)
	rose acetone*
15	terpinyl acetate
	4-isopropyl-1-methyl-2-[1'-propenyl]-benzene (Verdoracine, TM)
	yara*
	(4-isopropylcyclohexadienyl)ethyl formate

20 Examples of fragrance materials which lie within category B, but have Kovats index above 1600 and so are outside category B' are listed in the following table:

	Within category B but outside category B'
25	amyl cinnamate
	amyl cinnamic aldehyde
	amyl cinnamic aldehyde dimethyl acetal
	cinnamyl cinnamate

5	1,2,3,5,6,7,8,8a,-octathyro-1,2,8,8-tetramethyl-2-acetyl naphthalene (iso E super (TM))
	cyclo-1,13-ethylenedioxytridecan-1,13-dione (ethylene brassylate)
	cyclopentadecanolide (Exaltolide, TM)
	hexyl cinnamic aldehyde
10	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]- 2-benzopyran (Galaxolide, TM)
	geranyl phenyl acetate
	6-acetyl-1-isopropyl-2,3,3,5-tetramethylindane (Traseolide, TM)
	1,1,2,4,4,7-hexamethyl-6-acetyl-1,2,3,4- tetrahydronaphthalene (Tonalid, TM)

15 As indicated above, it is particularly preferred to utilise a perfume composition which has deodorant properties. Preferably, the perfume is a deodorant perfume giving a Malodour Reduction Value of at least 0.5, preferably at least 0.9, in the Malodour

20 Reduction Value test described below and which is an adaptation of the test described in EP-A-147191 and corresponding US-A-4663068.

The Malodour Reduction Value Test

In this test, the Malodour Reduction Value

25 of a deodorant perfume is measured by assessing its effectiveness, when applied to fabric, in reducing body malodour when the fabric so treated is placed in

contact with the axillae (armpits) of a panel of human subjects, and held there for a standard period of time. From subsequent olfactory evaluation by trained assessors, a Malodour Reduction Value can be
5 calculated so giving a measure of the effectiveness as a deodorant of the perfume under test.

Stage 1 is preparation of the perfume treated fabric. A test fabric is subjected to a textile finishing which applies perfume to the fabric
10 at a predetermined percentage of perfume composition, by weight of the cloth. A control fabric is given similar treatment, with or without perfume, depending on the purpose of the test. Depending on the purpose of the test, the fabrics may subsequently be washed
15 and dried.

The test and control fabrics are cut into 20cm x 20cm squares for testing.

Stage 2 is the carrying out of the test. A team of three Caucasian female assessors of minimum
20 age 20 years is selected to carry out olfactory evaluation on the basis that each is able to rank correctly the odour levels of the series of standard aqueous solutions of isovaleric acid listed below, and each is able to assign a numerical score,
25 corresponding to the odour intensity of one of these solutions, to the body malodour of a shirt insert

after has been worn in the axillary region by a male subject for a standard period of time.

A panel of 40 human subjects for use in the test is assembled from Caucasian male subjects of age within the range of from 20 to 55 years. By screening, subjects are chosen who develop axillary body malodour that is not unusually strong and who do not develop a stronger body malodour in one axilla compared with the other. Subjects who develop unusually strong body malodour, for example due to a diet including curry or garlic, are not selected for the panel.

For two weeks before the start of the test, the panel subjects are assigned an unperfumed, non-deodorant soap bar for exclusive use when washing and are denied the use of any other type of deodorant or antiperspirant. At the end of this period, the 40 subjects are randomly divided into two groups of 20.

The "test" and "control" fabric pieces are then tacked into 40 clean cotton or polyester cotton shirts in the underarm region in such a manner that in 20 shirts, the control fabric pieces are attached inside the left underarm region, and the test fabric pieces are attached in the right underarm region. For the remaining 20 shirts, the placing of control and test pieces of fabric is reversed.

The shirts carrying the tacked-in fabric

inserts are then worn by the 40 panel members for a period of 5 hours, during which time each panellist performs his normal work function without unnecessary exercise.

5 After this five hour period, the shirts are removed and the inserts detached and placed in polyethylene pouches prior to assessment by the trained panel of assessors.

 The malodour intensity of each fabric insert
10 is evaluated by all three assessors who, operating without knowledge of which inserts are "test" and which are "control" and, without knowing the scores assigned by their fellow assessors, sniff each fabric piece and assign to it a score corresponding to the
15 strength of the odour on a scale from 0 to 5, with 0 representing no odour and 5 representing very strong odour.

 Standard aqueous solutions of isovaleric acid which correspond to each of the scores 1, 2, 3, 4
20 and 5 are provided for reference to assist the assessors in the malodour evaluation. These are shown below:

SCORE	ODOUR LEVEL	CONCENTRATION OF AQUEOUS ISOVALERIC ACID (ML/L)
0	NO ODOUR	0

5

1	SLIGHT	0.013
2	DEFINITE	0.053
3	MODERATE	0.22
4	STRONG	0.87
5	VERY STRONG	3.57

The scores recorded by each assessor for each fabric piece are averaged. The average score of the "test" fabric pieces is deducted from the average score of the "untreated" control fabric pieces to give a Malodour Reduction Value.

As a check that the selection of panel subjects is satisfactory for operation of the test, the average score with unperfumed fabric pieces should be between 2.5 and 3.0.

Preferred deodorant perfumes are those which have a Malodour Reduction Value of at least 0.50, or 0.70, or 1.00. The higher the minimum value, the more effective is the perfume as a deodorant as recorded by the assessors in the Malodour Reduction Value Test. It has also been noted that consumers, who are not trained assessors, can detect by self-assessment a noticeable reduction in malodour on soiled fabric such as shirts and underclothes where the Malodour Reduction Value is at least 0.30, so the higher the Malodour Reduction Value above this figure, the more

noticeable is the deodorant effect.

Selection of a combination of fragrance materials to give a deodorant effect is explained in patents such as US-A-430679 referred to earlier.

5 Further systems of selection are given in US-A-5482635 and US-A-5554588 also mentioned above.

Such selections can be carried out using materials with preferred values of partition coefficient and Kovats index as discussed above.

10 US-A-5501805 describes perfume compositions made from a combination of fragrance materials, where the composition is a deodorant perfume yet has a relatively low odour. Such "low-odour" deodorant perfumes may be used in the present invention.

15 When this test is used to assess the deodorant effectiveness of a perfume composition, applied to fabric in accordance with this invention, the test fabric is a blend of 95% by weight cotton and 5% by weight spandex fibres. The control fabric is
20 100% cotton. The test and control fibres are selected to be similar in other respects, in particular to have the same weight per unit area.

The test fabric is subjected to treatment with a fabric finishing liquor, containing perfume, so
25 as to apply 0.5% of the perfume, by weight of the fabric. The control fabric is treated similarly, but

without perfume.

The test and control fabrics are not subsequently washed before testing.

However, this test procedure can be operated
5 in other ways. To demonstrate the higher deposition of perfume on spandex fibres, the control and test fabrics are both treated with the same fabric finishing liquor containing perfume. To isolate the deodorant effect of the perfume, the test and control
10 fabrics can be the same, but no perfume is present in the liquor used to treat the control fabric.

Example 1

This model experiment demonstrates perfume deposition on spandex fibres. A mixture of perfume
15 ingredients was prepared and added to an unperfumed, but otherwise conventional, laundry detergent powder, to provide a perfume concentration of 0.5% by weight.

The perfumed powder was used to wash test cloths which had not previously been treated with any
20 perfume. These were either all cotton, or 95% cotton with 5% spandex. After washing, the cloths were rinsed and then line dried overnight.

The perfume was extracted from the dry cloths with organic solvent, and the content of the
25 perfume ingredients in the solvent extracts was determined by gas chromatography. If the concentration

of an ingredient extracted from the spandex-containing cloth was greater than from the all-cotton cloth by a factor of 5 to 20, the result was coded as a medium enhancement (M). If the concentration was greater by 20 or more, it was coded high (H) and if less than 5 or not measurable, it was coded (L). The results obtained were as follows:

	Ingredient	K*	logP* *	Enhancement	Category
	Boisambrene Forte	1714	5.5	M	B
10	benzyl acetone	1206	2.0	M	-
	citronellol	1209	3.6	H	A'
	2,6-dimethyl-heptan-2-ol	975	2.9	L	-
	jasmacyclene	1394	2.9	H	B'
15	methyl salicylate	1167	2.3	L	-
	2-phenylethanol	1087	1.4	L	-
	terpinyl acetate	1331	4.0	H	B'
	tetrahydrogeraniol	1180	3.6	H	A'
	tetrahydrolinalol	1083	3.5	H	A'
20	Tonalid	1840	6.4	M	B
	yara	1416	3.2	H	B'

* Measured on OV-1 polydimethylsiloxane (Ohio Valley) as stationary phase using capillary gc

** Measured or estimated using 'logP' software from ACD
25 Inc.

Example 2

Cloth composed of 90% cotton, 10% spandex was treated in a fabric finishing step, using conventional equipment. Other cloth, consisting of cotton only, was treated in the same way. In both cases, the fabric finishing treatment was carried out for a period of 20 minutes, using an MCS jet machine (Urgano, Italy). The finishing liquors were applied applied at a liquor to cloth ratio of 20:1, at 40°C with a pH of 5.5. These liquors all contained Ceranine HCS (a finishing agent made by Sandoz) at a concentration such that this agent was applied to fabric at 1% by weight of the fabric.

The treatment liquors also contained perfume at varying concentrations, so that this was applied to the fabric at concentrations of 0.01%, 0.1% and 1% by weight of the fabric. Liquor without perfume was used to provide a control.

The perfume was used, designated "perfume U" contained 33.5% (by weight of the perfume composition) of fragrance materials in category A above, all of which had Kovats indices of 1050 to 1600 and therefore all fell within category A'. The perfume also contained 41.1% (by weight of the perfume composition) of materials in category B. These were made up from 26.7% with Kovats index over 1600 and 14.4% with

Kovats index of 1300 to 1600, so as to fall within category B'.

The cloths were then washed repeatedly, using a commercial detergent powder which included a different perfume. The washes were carried out using a Miele washing machine on its "Quickwash" programme at 40°C. 110gm of detergent powder was used for each wash. The fabric was rinsed three times after each wash and tumble dried.

The dried cloths were examined by a panel of expert assessors of perfume intensity. This was to determine the intensity of perfume on the fabric, but not its deodorant property. The results obtained were as follows:

	Odour Evaluation Scores					
	100% cotton			90% cotton and 10% spandex		
Washes:	1	3	5	1	3	5
Perfume U						
0%	2.0	2.4	2.8	4.0	4.4	4.6
1.0%	6.4	3.6	<3	16.0	14.0	12.8
0.1%	3.6	<3	<3	10.4	9.7	9.0
0.01%	3.2	<3	<3	8.8	8.0	7.2

It can be seen that the cloths which were not perfumed in the finishing treatment took up

perfume in the first wash and this perfume built up slowly in subsequent washes. The quantity of perfume taken up was greater on the cloth which included spandex fibres.

5 The cloths containing spandex fibres which were perfumed during the finishing treatment had a much higher level of perfume on them after one wash than the 100% cotton cloths. Even after five washes, the intensity of perfume on them exceeded the intensity
10 of perfume on the 100% cotton cloths after one wash, and on the cloths which had not been perfumed prior to the first wash. Thus the spandex fibres were providing enhanced retention of perfume as well as enhanced deposition.

15 The 100% cotton cloths which had been perfumed during the finishing treatment were assessed again after 3 and 5 washes. The results showed that the level of intensity of the perfume was less than that observed after 1 wash but also showed that the
20 olfactive differences between perfume U used in the finishing treatment and the perfume present in the washing powder was confusing the panellists.

Example 3

Two deodorant perfumes were used in
25 treatment of cloths by a finishing process as in Example 2.

Perfume L contained materials in the above categories as follows:

- Category A: 30 wt% (all with Kovats index above 1600)
- 5 Category B: 68.5 wt% (13% with Kovats index 1300-1600 and therefore within category B', and 55.5 wt% with Kovats index above 1600).

Perfume M contained materials in the above categories as follows:

- 10 Category A: 24.9 wt% (16.3 wt% with Kovats index 1050-1600 and therefore within category A', and 8.6 wt% with Kovats index above 1600)
- 15 Category B: 55.3 wt% (8.6 wt% with Kovats index 1300-1600 and therefore within category B', and 46.7 wt% with Kovats index above 1600).

The test cloths were: 100% cotton, 90% cotton with 10% spandex, 95% cotton with 5% spandex, 100% nylon and 82% nylon with 18% spandex. Perfume was used at a concentration of 0.5% based on the weight of the fabric. The treated cloths were tested for Malodour reduction in the test described earlier. The control cloths were 100% cotton, which had been subjected to the same finishing treatment, but without

perfume in that finishing treatment. The results are set out in the following tables, which show substantial enhancements of malodour inhibition when fabrics containing spandex fibres were used.

5 Test 1:

	Fabric		perfume M (% by weight of fabric)	Malodour score	Malodour reduction	Malodour reduction as % of control
	other fibre	spandex				
10	90% cotton	10%	0.5%	1.19	1.46	55%
	100% cotton	0	0.5%	1.92	0.73	27.4%
	82% nylon	18%	0.5%	1.00	1.65	62.1%
15	100% nylon	0	0.5%	1.97	0.68	25.5%
	100% cotton (control)	0	0	2.65		

Notes: % malodour reduction calculated as 100%

20
$$\times (\text{control score} - \text{sample score}) / \text{control score}$$

Statistical calculation showed that a difference in malodour reduction of 6.9% was significant at 95% level of confidence.

Test 2:

	Fabric		perfume (% by weight of fabric)	Malodour score	Malodour reduction	Malodour reduction as % of control
	other fibre	spandex				
5	95% cotton	5%	0.5% L	1.15	1.22	51.5%
	95% cotton	5%	0.5% M	1.29	1.08	45.6%
10	100% cotton (control)	0	0	2.37		

Note: Statistical calculation showed that a difference in malodour reduction of 6.3% was significant at 95% level of confidence.

15 In test 1, malodour scores on 100% cotton fabric, with and without perfume, demonstrate a malodour reduction value of 0.73 attributable to the perfume. A similar malodour reduction value was observed when the test cloth was 100% nylon.

20 When spandex fibre was incorporated, the malodour reduction increased greatly, showing that increased deposition of perfume on spandex fibres compared with other fibres also provides an increased deodorant efficiency.

25 In test 2, similar high values of malodour reduction were obtained when either perfume L or

perfume M was used, in test fabrics with 5% by weight spandex fibres.

CLAIMS

1. A method of treating textile which is yarn or unworn fabric containing spandex fibres, comprising contacting the textile with a perfume composition
5 which is a mixture of fragrance materials, so that fragrance materials are deposited on the textile.
2. A method according to claim 1 wherein the textile contains from 0.5 wt % to 50 wt % spandex fibres and the amount of fragrance materials deposited
10 on the textile is from 0.001% to 1% by weight of the textile.
3. A method of treating a spandex fibre comprising contacting the fibre with a perfume composition which is a mixture of fragrance materials, so that fragrance
15 materials are deposited on the spandex fibre.
4. A method according to claim 1, claim 2 or claim 3 wherein the perfume composition contains at least 50%, by weight of the perfume composition, of fragrance materials selected from:
20 Category A) hydroxylic materials which are alcohols, phenols or salicylates, with an octanol/water partition coefficient (P) whose common logarithm ($\log_{10}P$) is 2.5 or greater, and a gas chromatographic Kovats index (as
25 determined on polydimethylsiloxane as non-polar

stationary phase) of at least 1050, and

Category B) esters, ethers, nitriles, ketones or aldehydes, with an octanol/water partition coefficient (P) whose common logarithm ($\log_{10}P$) is 2.5 or greater, and a gas chromatographic Kovats index (as determined with polydimethylsiloxane as non-polar stationary phase) of at least 1300.

5. A method according to claim 4 wherein the perfume composition contains at least 10%, by weight of the perfume composition, of fragrance materials selected from:

Category A') hydroxylic materials which are alcohols, phenols or salicylates, with an octanol/water partition coefficient (P) whose common logarithm ($\log_{10}P$) is 2.5 or greater, and a gas chromatographic Kovats index (as determined on polydimethylsiloxane as non-polar stationary phase) lying within the range 1050 to 1600, and

Category B') esters, ethers, nitriles, ketones or aldehydes, with an octanol/water partition coefficient (P) whose common logarithm ($\log_{10}P$) is 2.5 or greater, and a gas chromatographic

Kovats index (as determined on polydimethylsiloxane as non-polar stationary phase) lying within the range 1300 to 1600.

6. A method according to claim 4 wherein the
5 perfume composition contains at least 70%, by weight of the perfume composition, of fragrance materials selected from categories A and B, which materials include at least 25% by weight of the perfume composition, of fragrance materials from the
10 categories A' and B' defined in claim 4.

7. A method according to claim 6 wherein the perfume composition contains at least 80%, by weight of the perfume composition, of fragrance materials selected from categories A and B, which materials
15 include at least 40%, by weight of the perfume composition, from categories A' and B'.

8. The method of claim 1, wherein the textile is contacted with the perfume composition in a fabric finishing step.

20 9. A textile which is yarn or unworn fabric and which contains spandex fibres, having fragrance materials deposited on the textile.

10. A textile according to claim 9 which contains from 0.5 to 50 wt % spandex fibres and the amount of
25 fragrance materials deposited thereon is from 0.001% to 1% by weight of the textile.

11. A textile according to claim 9 or claim 10 which is yarn, a fabric web or length thereof, or an unworn garment.
12. A textile which comprises spandex and other
5 fibres and which has fragrance materials preferentially deposited on the spandex fibres.
13. A spandex fibre having fragrance materials deposited on the spandex fibre.
14. Use of a perfume composition which is a mixture
10 of fragrance materials in the treatment of yarn or unworn fabrics containing spandex and other fibres, to deposit fragrance materials on the spandex fibres.

INTERNATIONAL SEARCH REPORT

Int. lional Application No

PCT/GB 98/03056

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D06M13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 596 792 A (UNILEVER LTD) 26 August 1981 see claims ---	1,3,9, 12-14
A	DE 296 00 628 U (WERN LEMPERT CORNELIA ;OELLIG ALEXANDER (DE)) 15 May 1997 see the whole document ---	1,3,9, 12-14
A	DE 40 11 928 A (CHAMBET MONIKA) 27 June 1991 see the whole document ---	1,3,9, 12-14
A	DE 42 42 327 A (BEGGEL KLAUS) 16 June 1994 see the whole document ---	1,3,9, 12-14
-/--		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Herrmann, J

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.
PCT/GB 98/03056

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 581 274 A (MATSUI SHIKISO KAGAKU KOGYOSH0) 2 February 1994 see claims ---	1,3,9, 12-14
A	WO 93 14259 A (JASPER GMBH) 22 July 1993 see page 6, paragraph 2 see claims ---	1,3,9, 12-14
A	DATABASE WPI Section Ch, Week 8949 Derwent Publications Ltd., London, GB; Class A87, AN 89-361939 XP002090301 & JP 01 272875 A (KANEBO LTD) , 31 October 1989 see abstract ---	1,3,9, 12-14
A	DATABASE WPI Section Ch, Week 9426 Derwent Publications Ltd., London, GB; Class A25, AN 94-211413 XP002090302 & JP 06 146112 A (NISSHINBO IND INC) , 27 May 1994 see abstract ---	1,3,9, 12-14
A,P	EP 0 841 391 A (PROCTER & GAMBLE) 13 May 1998 see page 12, line 35 - page 18, line 13 -----	1,3,9, 12-14

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 98/03056

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1596792 A	26-08-1981	HK 42084 A	18-05-1984
DE 29600628 U	15-05-1997	NONE	
DE 4011928 A	27-06-1991	NONE	
DE 4242327 A	16-06-1994	NONE	
EP 0581274 A	02-02-1994	JP 6093570 A	05-04-1994
		AU 4428493 A	03-02-1994
		CA 2101601 A	01-02-1994
		FI 933380 A	01-02-1994
WO 9314259 A	22-07-1993	DE 4200352 A	19-08-1993
		CZ 9401640 A	16-11-1994
		EP 0620875 A	26-10-1994
EP 0841391 A	13-05-1998	WO 9820102 A	14-05-1998